

Voltametric Behavior of Noradrenaline at 2-Mercaptoethanol Self-Assembled Monolayer Modified Gold Electrode and its Analytical Application

XiuHua Zhang and ShengFu Wang*

Faculty of Chemistry and Material Science, Hubei University, Wuhan 430062, China

*Author to whom correspondence should be addressed. E-mail: wangsf@hubu.edu.cn

Received: 14 January 2003 / Accepted: 12 February 2003 / Published: 21 February 2003

Abstract: 2-Mercaptoethanol self-assembled monolayer (ME/Au SAMs) was prepared on a gold electrode. The ME/Au SAMs was characterized by using ATR-FTIR and dynamic contact angle measurements. The electrochemical behaviors of noradrenaline (NE) on the ME/Au SAMs were studied in BR buffer solution. The modified electrode accelerated electron transfer rate of the redox of NE and showed an excellent electrocatalytic activity. The diffusion coefficient (D) of NE was obtained to be $4.3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The catalytic current increased linearly with the concentration of NE in the range of 2.0×10^{-6} - 1.0×10^{-3} M by square wave voltammetry response. The modified electrode could eliminate the interference of ascorbic acid (AA) at 40-fold concentration of NE and could be satisfactorily used for the determination of NE in the drug injection.

Keywords 2-mercaptoethanol (ME), Self-assembled monolayers (SAMs), Square wave voltammetry (SWV), Noradrenaline (NE)

Introduction

Nowadays much attention has been focused on the self-assembled monolayers modified electrode in the fields of electrochemistry and electroanalytical chemistry. In particular the self-assembly of organosulfur compound on gold surfaces have been extensively studied^[1-4]. By the strong S-Au bond, the thiol molecules are link to gold electrode surface, thus, forming self-assembled monolayers. These modified surfaces exhibit new electrochemical and physical properties that are from the organic monolayer. The functionalization of SAMs has also been reported as a means for various applications^[5-8].

The recent development of various surface characterization techniques has proved the well-ordered surface structure of long-chain thiols and other thiol derivatives^[9,10]. In contrast to the considerable attention paid to the surface structure characterization and analytical applications of long-chain monolayer assemblies, there seem to be few reports on the electrochemical application of short-chain self-assembled monolayers. Takehara and Ide had investigated the electrochemical properties of the short-chain self-assembled monolayers by cyclic voltammetry^[11,12]. Kudelski^[13] and Tarabara et al.^[14] research groups had studied the surface structure of short-chain self-assembled monolayers on silver electrode by Surface-enhanced Raman Scattering (SERS).

Previously, our research groups had reported the SAMs modified by short-chain thiols for determination catechols and catecholamines^[15-17]. As a continuation of our work, the shortest-chain thiol compound that is 2-mercaptoethanol (ME) has been used as the modifying molecule of SAMs and the ME/Au SAMs have been successfully prepared on the bare gold electrode. ATR-FTIR and dynamic contact angle measurements have been used for the characterization of the films. The electrochemical behavior of noradrenaline (NE) was investigated on ME/Au SAMs modified electrode.

NE is also one of the derivatives of catecholamines that are secreted by the adrenal medulla, existing as an organic cation in the nervous tissue and biological body fluid^[18]. It plays important physiological roles in the central nervous system. It affects muscle and tissue control, simulates arteriole contraction, decreases peripheral circulation, activates lipolysis in adipose tissue, thus, it is necessary to develop a quantitative determination method of NE for studying its physiological function and the diagnosis of some diseases in clinical medicine. The determination and voltammetric behaviors of NE on modified electrode have been reported before^[19,20]. The ME/Au SAMs prepared in this work has a distinct electrocatalytic effect on NE and the reductive peak current has a good linear relation with NE concentration by square wave voltammetry (SWV). We found that ascorbic acid (AA) had no reductive peak within potential range we investigated on ME/Au SAMs modified electrode, it could eliminate efficiently the interference of AA in determination of NE. Satisfactory results were obtained by using this modified electrode for analyzing real samples.

Experimental

Apparatus and Chemicals

Electrochemical measurements were carried out on CHI630A (U.S.A). A three-electrode system was used in the measurements, with a bare gold electrode (diameter 2mm) or β -mercaptoethanol self-assembled monolayers modified gold electrode (i.e. ME/Au SAMs) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode. Spectrum One FTIR spectrophotometer (Perkin Elmer, USA) was used to achieve the ATR-FTIR spectra of ME/Au SAMs at a resolution of 4 cm^{-1} over the $4000\text{ -}600\text{ cm}^{-1}$ spectral region. The contact angle was performed using K121 Contact Angle- and Adsorption Measuring System (KRÜSS GMBH, Germany) by plate method.

2-Mercaptoethanol was purchased from Sigma (USA) and noradrenaline (NE) from Fluka (Switzerland). All chemicals were of analytical-reagent grade. All solutions were prepared with pure

water. The noradrenaline bitartrate injection was obtained from Wuhan Pharmaceutical Factory (Hubei province, China).

Preparation of ME/Au SAMs

Prior to modification, the gold electrodes were polished with Al_2O_3 slurry on microcloth pads, and then rinsed with pure water and ultrasonicated in absolute ethanol and in pure water for 10 min each. Then it was pretreated by heating in piranha solution (7:3 mixture of concentrated sulfuric acid and 30% hydrogen peroxide) at 90°C for 15 min in order to remove possible contaminants, rinsed with pure water and sonicated in absolute ethanol and in pure water for 10 min each. Residual contaminants on bare gold can be removed by scanning in the potential from 0 to 1.5 V versus SCE in diluted (1.0 M) sulfuric acid at 0.1 V s^{-1} until a constant background cyclic voltammetry curve was obtained.

The freshly pretreated electrode was immersed in 50 mg ml^{-1} 2-mercaptoethanol ethanolic solution for 24 h. The electrodes were ready for use after they were rinsed with pure water and dried under nitrogen atmosphere at room temperature.

Results and Discussion

ATR-FTIR Characterization of ME/Au SAMs

Fig.1 shows the ATR-FTIR spectra of β -mercaptoethanol (1a) and β -mercaptoethanol film modified gold electrode (1b). In contrast with the two spectra, the most important difference between them can be observed by the fact that the band at 2555 cm^{-1} of -SH in Fig.1a was disappeared in Fig.1b. It is attributed to the cleavage of S-H bond and the formation of a new bond, i.e., S-Au bond. This phenomenon proves the fact that β -mercaptoethanol has been assembled on the gold electrode. What's more, the bands at 2873 cm^{-1} and 2932 cm^{-1} of vibration of -CH₂- in Fig.1a existed clearly in Fig.1b. These facts prove further that the bond of S-Au is strong, other groups in the β -mercaptoethanol molecule don't affect its assembling.

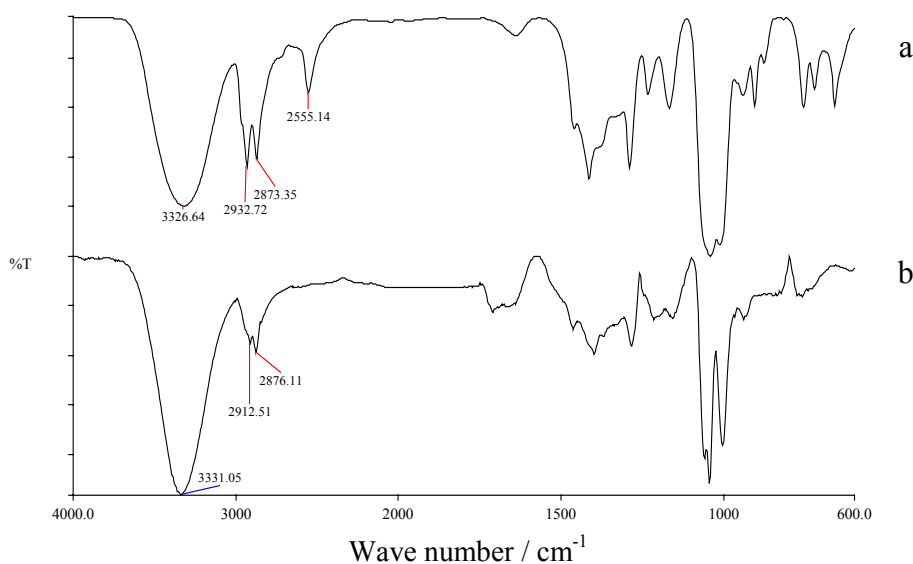


Figure 1. ATR-FTIR spectra of 2-mercaptoethanol (a) and ME/Au SAMs (b).

Contact Angle Determination of ME/Au SAMs

Figure 2 shows the variation of advancing contact angle of ME/Au SAMs as a function of assembling time in water. From the graph, we can conclude that the contact angle decline dramatically within 50 min and then tend to stability when the assembling time excess 100min, which indicate the assembling rate of 2-mercaptoethanol on gold is obviously lower than that of long-chain thiols which were reported before [21,22]. Since the hydrophilicity of the hydroxyl group in 2-mercaptoethanol, the surface of the assembled monolayers is completely hydrophilic. The change trend of the contact angle shows the dynamic process that the degree of 2-mercaptoethanol covering on the surface of gold increased gradually and reached saturation at last. The results of the contact angle also verifies that 2-mercaptoethanol formed self-assembled monolayers on the gold surface.

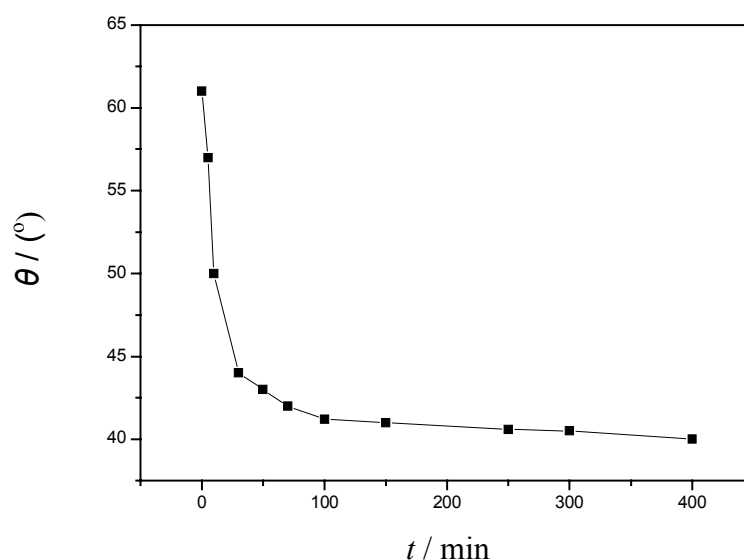


Figure 2. Plot of advancing contact angle of ME/Au SAMs vs. assembling time.

Voltammetric Behaviors of the ME/Au SAMs

No redox peak current was recorded by cyclic scanning with the potential range from 0 to 0.6 V in BR buffer of pH=5.5. Compared with the bare gold electrode, its background current drops greatly. That's because the stable modified monolayer of 2-mercaptoethanol formed by S-Au bond on the surface of gold electrode brought down the electron transfer rate between the surface of the electrode and the buffer [23].

Electrocatalytical Behaviors of NE at ME/Au SAMs

The electrochemical reaction process of NE at electrodes can be written as below [24]:

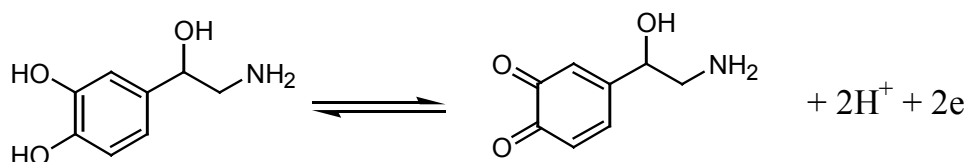


Fig.3 shows the cyclic voltammograms of 1mM NE on bare gold electrode (a) and on ME/Au SAMs modified electrode (b). It can be seen that the presence of a SAMs of 2-mercaptoethanol at the electrode surface reduces the overvoltage of NE oxidation, shifting the E_{pa} value negatively by 189 mV. The peak current was enhanced about three times. Compared with the response of NE on the bare gold electrode, the ME/Au SAMs modified electrode exhibited obviously higher current response towards NE redox. The peak separations between the anodic and cathodic peak of NE, ΔE_p were 104 mV for the ME/Au SAMs modified electrode and 344 mV for the bare gold. Since the -OH group is the electroactive group in NE and is present in much closer vicinity of the ME/Au SAMs modified electrode though O H—O bond than the bare gold electrode, this might lead to much fast kinetics of NE redox on the ME/Au SAMs modified electrode.

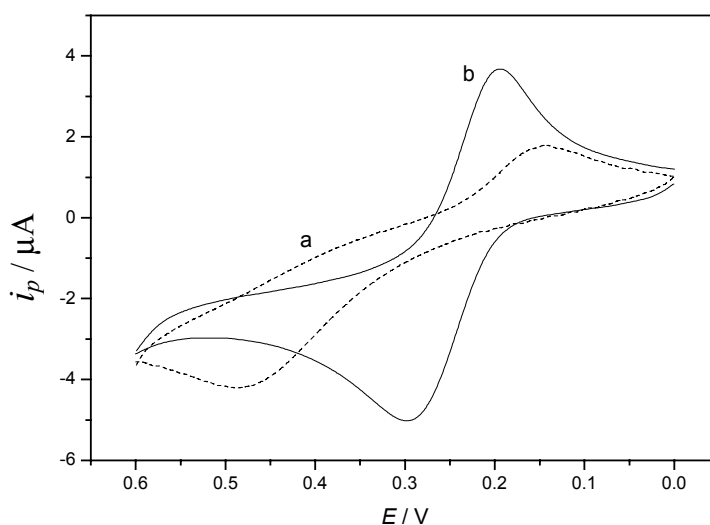


Figure 3. Cyclic voltammograms of 1.0 mM NE on bare gold electrode (a) and on ME/Au SAMs modified electrode (b) in B-R buffer (pH 5.5) at a scan rate of 50 mV s^{-1} .

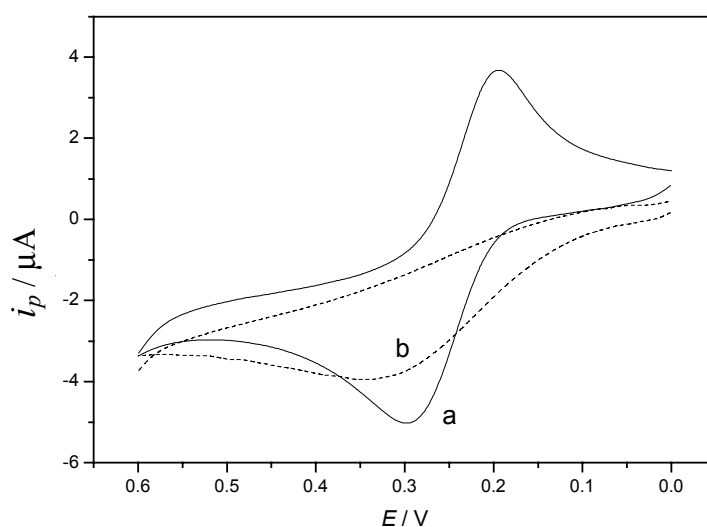


Figure 4. Cyclic voltammograms of 1.0 mM NE (a) and 1 mM AA (b) on ME/Au SAMs in B-R buffer (pH 5.5) at a scan rate of 50 mV s^{-1} .

The reductive peak current increased with the increase of scan rate on ME/Au SAMs in pH5.5 BR buffer, and exhibited a linear relation to the square root of the scan rate in the scan rate range 3-300 mV/L with the regression equation $i_{pc}=3.3614v^{1/2}+11.371$ ($i_{pc}:10^{-8}A$, $v:mV s^{-1}$) and a correlation coefficient of 0.9982, indicating a fast electrocatalytic reaction and the electron transfer was controlled by the diffusion of redox species. According to Randles formula^[25]: $i_p=2.69\times 10^5 n^{3/2} AD^{1/2} v^{1/2} C$, we can calculate the diffusion coefficient D of NE was $4.3\times 10^{-8} cm^2 s^{-1}$.

In order to eliminate the interference of AA in determination of NE, we also analysed the electrochemical behaviors of AA on ME/Au SAMs. From Fig.4 we can find that there was no reductive peak of AA on ME/Au SAMs, which indicated that AA don't interfere in determination of NE. We detected the reductive peak in determination of NE in the subsequent experiments.

The Effect of pH on Peak Current of NE

The effect of pH on the reductive peak was investigated by cyclic voltammetry. As shown in Fig. 5, reductive peak current varied with the pH value and reached a maximum at pH=5.5. So the determination of NE was performed in BR buffer of pH5.5.

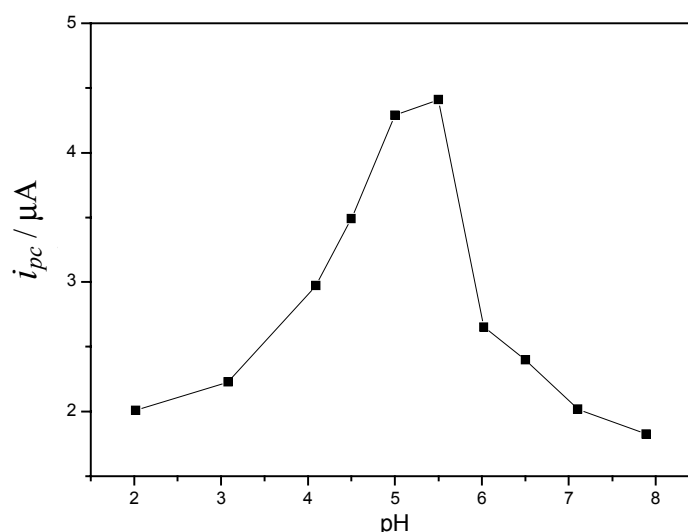


Figure 5. The effect of pH on i_{pc} of 1.0 mM NE.

Analytical Applications

The possibility of using the ME/Au SAMs modified electrodes for the determination of NE in practical samples was tested. Under the optimum conditions chosen, the SWV peak height was linearly related to the NE concentration within the range 2.0×10^{-6} - 1.0×10^{-3} M. Fig. 6 shows the SWV obtained for NE in the concentration range from 2.00×10^{-6} to 1.00×10^{-4} M. The linear regression equation was $i_{pc}=6.816c+0.3184$ ($i_{pc}/10^{-7}A$, $c/10^{-4} M$) and the correlation coefficient was 0.9984. The detection limit (three times the signal blank/slope) was 7.0×10^{-7} mol /L. The relative standard deviation was 1.2% for solution containing 1.0×10^{-5} M NE (n=11).

After AA or glucose was added into the cell containing 8.0×10^{-5} M NE, The signal of SWV did not change up to 40 or 1000-fold of the concentration of NE, respectively, indicating that AA or glucose

did not interfere. The modification of the electrode can efficiently eliminate their interference. At the same time, K^+ , Na^+ , Ca^{2+} , Al^{3+} , NH_4^+ , Cl^- , PO_4^{3-} , SO_4^{2-} and Ac^- did not interfere and S^{2-} , Fe^{2+} and NO_2^- interfered seriously the determination. The dopamine (DA) and adrenaline (EP), which are electroactive, often coexist with NE in biological system, and they can be redox at a potential near that of NE, resulting in an overlapping voltammetric response.

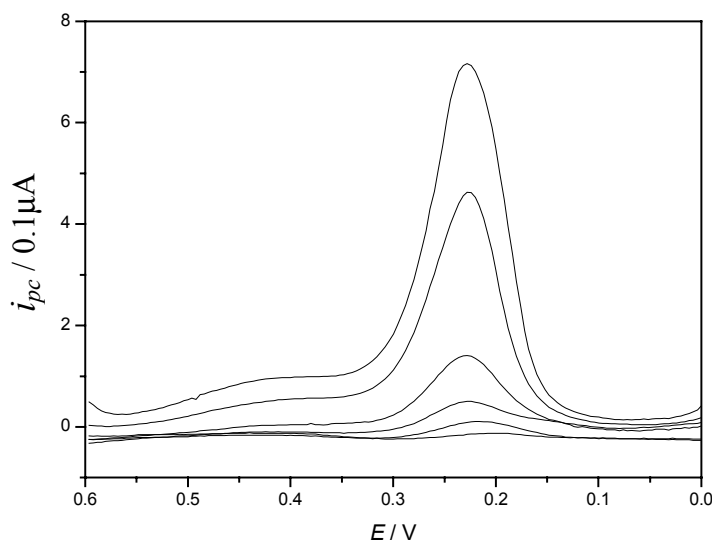


Figure 6. SWV graphs of NE at different concentrations (from bottom to top): 2.0, 6.0, 10.0, 20.0, 60.0, 100 μ M.

NE in injection of noradrenaline bitartrate injection (Wuhan Pharmaceutical Factory, P.R.C) was determined by the calibration curve method with the ME/Au SAMs modified electrode. The average result of NE injection is 0.98 mg ml^{-1} , which is quite corresponding to the value that was given by injection specification (1.00 mg ml^{-1}). Recoveries of 95.54% and 103.9% of NE from the injection NE samples were obtained using the modified electrode. In this study, differential standard concentrations of NE were added to diluted NE injection, respectively. Table 1 shows the result of the recoveries test. The good agreement with the method is a promising feature for the applicability of the modified electrode for direct determination of NE in real samples.

Table 1. Result of recoveries of NE.

Samples/ 10^{-3} mg	Added/ 10^{-3} mg	Found/ 10^{-3} mg	Recoveries (%)
	2.568	11.409	99.65
	3.853	12.582	96.87
8.850	5.137	13.758	95.54
	6.421	15.310	100.6
	10.274	19.525	103.9
	12.843	21.491	98.43

Acknowledgement

The work was supported by Natural Science Foundation of Hubei province of P. R. China (2000J007).

References

1. Dubois, L.H.; Nuzzo, R.G. Synthesis. *Annu. Rev. Chem.* **1992**, *43*, 437.
2. Hsueh, C.C.; Liu, Y.; Henry, M.; Freund, M. S. *Anal. Chim. Acta* **1999**, *397*, 135.
3. Gadzekpo, V.P.Y.; Bühlmann, P.; Xiao, K.P.; Aoki, H.; Umezawa, Y. *Anal. Chim. Acta* **2000**, *411*, 163-173.
4. Poirier, G. E. *Chem. Rev.* **1997**, *97*, 1117.
5. Turyan, I.; Mandler, D. *Anal. Chem.* **1997**, *69*, 894.
6. Dalmia, A.; Liu, C. C.; Savinell, R.F. *J. Electroanal. Chem.* **1997**, *430*, 205.
7. Murthy, A.S.N.; Sharma, J. *Anal. Chim. Acta* **1998**, *363*, 215.
8. Ge, B.; Lisdat, B. *Anal. Chim. Acta* **2002**, *454*, 53.
9. Ulman, A.; Evans, S.D.; Shnidman, Y.; Sharma, R.; Eilers, J.E.; Chang, J.C. *J. Am. Chem. Soc.* **1991**, *113*, 1499.
10. Evans, S.D.; Sharma, R.; Ulman, A. *Langmuir* **1991**, *7*, 156.
11. Takehara, K.; Ide, Y. *Bioelectrochemistry and Bioenergetics* **1992**, *27*, 207.
12. Takehara, K.; Ide, Y. *Bioelectrochemistry and Bioenergetics* **1992**, *27*, 501.
13. Kudelski, A. *Surface Sci.* **2002**, *502-503*, 219.
14. Tarabara, V.V.; Nabiev, R.I.; Feofanov, V.A. *Langmuir* **1998**, *14*, 1092.
15. Wang, S.F.; Du, D.; Zou, Q.C. *Tanlanta* **2002**, *57*, 687.
16. Zhang, X.H.; Wang, S.F. *Anal. Lett.* **2002**, *35*, 995.
17. Zhang, X.H.; Wang, S.F. *Chinese J. Appl. Chem.* **2002**, *19*, 657.
18. Shen, T.; Wang, J.Y. *Biochemistry (the 2nd edition)*. Beijing, Higher Education Press 1990, p.427.
19. Fang, Y.Z.; Yu, Y.L.; He, P.G. *Anal. Chem.* **1995**, *67*, 1440.
20. Burnette, W.B.; Bailey, M.D.; Kukoyi, S. *Anal. Chem.* **1996**, *68*, 2932.
21. Zhao, W.J.; Yu, H.Z.; Wang, Y.Q.; Zhang, H.L.; Liu, Z.F. *Chinese Acta Phys. Chem.* **1997**, *13*, 42.
22. Bain, C.D.; Troughton, E.R.; Whitesides, G.M. *J. Am. Chem. Soc.* **1989**, *111*, 321.
23. Gu, K.; Zhu, J. J.; Chen, H.Y. *Chinese J. Anal. Chem.* **1999**, *27*, 1172.
24. Sun, Y.X.; Ye, B. X. *Chinese J. Anal. Chem.* **1998**, *26*, 506.
25. Durfor, C.N.; Yenser, B.A.; Bowers, M.L. *J. Electroanal. Chem.* **1988**, *244*, 287.

Sample Availability: Available from the authors.